1 **Supplementary Material**

2 In order to better define the variability of the end-members of the groundwater

3 discharged into the northern South China Sea (NSCS), we adopted the definition of

4 Moore (1999) regarding subterranean estuary (STE), which emphasized that the

5 discharge of groundwater is as a matter of fact through a STE before its export to the

6 shelf similar to a surface river estuary. This appendix provides additional description

7 for the sampling and distribution of the dissolved constituents in the NSCS STE.

8

9 **Groundwater Sampling**

10 We sampled coastal groundwater and spring water along the NSCS shelf in

11 December 2008 (red inverted triangle in Fig. 1) and October 2010 (blue triangle in

12 Fig. 1).

13 Groundwater was collected both from water-providing wells and in the intertidal

14 zone as close to the shoreline as possible using Push Point sampler (MHE Products,

15 Inc.). Sampling with a flojet$^{TM}$ pump was not initiated until stable readings of

16 salinity, pH and dissolved oxygen of the groundwater were recorded by a WTW 340i

17 Multi-Parameter Field Meter. The pump rate was maintained between 250-500 mL

18 min$^{-1}$ to minimize disturbance of the groundwater system. All of the groundwater

19 samples were collected at various depths within the unconfined surficial aquifer.

20

21 **Spatial variations of salinity and Ra isotopes in the NSCS subterranean estuary**

22 In 2008, there was no apparent spatial variation for the Ra quartet in fresh

1  groundwater with a mean of 13.6±1.69 dpm 100 $L^{-1}$ for $^{223}$Ra and a mean of

2  427±6.58 dpm 100 $L^{-1}$ for ex $^{224}$Ra (Table S1). Saline springs contained very high

3  $^{223}$Ra (60.5±15.6 dpm 100 $L^{-1}$) and ex $^{224}$Ra (1195±35.1 dpm 100 $L^{-1}$) compared with

4  fresh groundwater. The activities of the long-lived Ra isotopes in the fresh

5  groundwater (182±21.2 dpm 100 $L^{-1}$ for $^{226}$Ra and 581±31.1 dpm 100 $L^{-1}$ for $^{228}$Ra)

6  and the saline spring (161±21.9 dpm 100 $L^{-1}$ for $^{226}$Ra and 422±31.0 dpm 100 $L^{-1}$ for

7  $^{228}$Ra) were similar (Table S1). Two possible reasons may explain the contrast

8  between fresh and saline groundwater and between the Ra isotopes with different

9  half lives. First, all the Ra isotopes would be desorbed from particles with increasing

10  ionic strength. Second, if the spring was exposed to the seawater long enough for ion

11  exchange process to complete, Ra would be diluted by the low Ra seawater. This

12  removal process can reduce the long-lived Ra but not the short-lived Ra isotopes due

13  to the latter's fast regeneration rate from the sediments.

14  In the 2010 sampling, the brackish groundwater had higher short-lived Ra isotopes

15  (512-1718 dpm 100 $L^{-1}$ for ex $^{224}$Ra and 11.0-60.5 dpm 100 $L^{-1}$ for $^{223}$Ra) relative to

16  the fresh groundwater (61.7-897 dpm 100 $L^{-1}$ for ex $^{224}$Ra and 3.63-31.4 dpm 100 $L^{-1}$

17  for $^{223}$Ra). Long-lived $^{228}$Ra in fresh groundwater revealed a broader spatial variation,

18  ranging from 30.2 to 396 dpm 100 $L^{-1}$, lower by a factor of 3.5 on average than that in

19  brackish groundwater (in the range from 419 to 872 dpm 100 $L^{-1}$) in 2010 (Table S1).

20  Comparing the Ra activities in these two years, saline spring in 2008 had comparable

21  high short-lived Ra with brackish groundwater in 2010. The $^{223}$Ra and ex $^{224}$Ra in

22  fresh groundwater were close in 2008 and 2010, but with larger spatial variability in

1    2010 (Table S1). As presented in Fig 6C and Table S1, both fresh groundwater and

2    spring collected in 2008 had high $^{228}$Ra comparable with that in brackish groundwater

3    sampled in 2010 (with averages of 462 versus 568 dpm 100 L$^{-1}$), which was higher

4    than fresh groundwater in 2010 (averaging 160 dpm 100 L$^{-1}$). The $^{228}$Ra and $^{226}$Ra

5    activities in groundwater along the NSCS fell into the general range of long-lived Ra

6    in various coastal monitor wells over the continental margins (10-1730 dpm 100 L$^{-1}$

7    for $^{228}$Ra and 20-1740 dpm 100 L$^{-1}$ for $^{226}$Ra; Moore, 2010).

8    The $^{228}$Ra/$^{226}$Ra activity ratio (AR) ranged 2.63-7.82 with an average of 4.09 in the

9    groundwater collected in 2008 along the NSCS shelf. The higher $^{228}$Ra activity than

10   $^{226}$Ra can be explained by different $^{232}$Th/$^{238}$U ARs in the aquifer in view that $^{232}$Th

11   (the parent of $^{228}$Ra) can be preferentially adsorbed onto sediment than $^{238}$U (the

12   parent of $^{226}$Ra), and as such the sediment is a continuous $^{228}$Ra source for the

13   groundwater and spring (Swarzenski et al., 2003). Ra-223 and ex $^{224}$Ra in Fig. S1

14   showed good agreement in the $^{223}$Ra/ex $^{224}$Ra AR between the two years, indicating

15   the same $^{235}$U (the parent of $^{223}$Ra)/$^{232}$Th (the parent of $^{224}$Ra) ratio in the aquifers

16   along the shoreline of the NSCS shelf.

17

18   **Major ions (Na$^+$, Mg$^{2+}$, and Ca$^{2+}$) in the NSCS subterranean estuary**

19   Sodium and magnesium concentrations (Table S1) correlated linearly with salinity

20   (figures not shown), suggesting that the major ion composition was a result of the

21   mixing of seawater and fresh groundwater. Calcium showed slight addition from the

22   conservative mixing which may be explained by CaCO$_3$ dissolution and/or ion

1 exchange (Appelo, 1994; Harriet et al., 2004).

2 The fresh groundwater was the major source of DIN ($NH_4^+ + NO_3^- + NO_2^-$) and $SiO_4^{4-}$

3 (DSi) on the NSCS shelf as indicated by their distribution with salinity in both 2008

4 and 2010 (Table S1 and Figs. S2A-S2C). $NH_4^+$ concentration varied by three orders of

5 magnitude, from 0.3 to 318 μmol $L^{-1}$, in fresh groundwater (Table S1 and Fig. S2A)

6 with an average of 127 μmol $L^{-1}$. $NH_4^+$ was as high as 573 μmol $L^{-1}$ at salinity ~15.

7 $NO_3^- + NO_2^-$ was in the range from 87.6 to 1612 μmol $L^{-1}$ in the fresh groundwater

8 (Table S1 and Fig. S2B) and decreased to 5.6 μmol $L^{-1}$ at salinity of 24.3, indicating

9 removal during mixing with seawater. $SiO_4^{4-}$ was in the range from 83.0 to 702 μmol

10 $L^{-1}$ in the fresh groundwater with average 292 μmol $L^{-1}$ and correlated positively with

11 salinity, as found elsewhere such as in the West Neck Bay STE (Beck et al., 2007).

12 However, $PO_4^{3-}$ concentrations in most of the groundwater were low, averaging 1.0

13 μmol $L^{-1}$, except three samples with extremely high $PO_4^{3-}$ concentrations of 17.2, 19.8

14 and 37.4 μmol $L^{-1}$, respectively. Note that, of the three exceptions, one was from a

15 freshwater well, and the other two were brackish groundwater (salinity ~15).

16 Generally speaking, nitrogen and phosphate concentrations in groundwater are low

17 when derived from natural sources, namely *in situ* organic matter decay and mineral

18 weathering (Slomp and Van Cappellen, 2004). The large spatial variation of DIN in

19 fresh groundwater suggests multiple N sources. High DIN concentrations might be

20 affected by anthropogenic activity such as fertilizer, manure and sewage, especially

21 aquaculture wastewater (Cao et al., 2007). Excess $NH_4^+$ and $PO_4^{3-}$ but depletion of

22 $NO_3^- + NO_2^-$ during the mixing of seawater and groundwater (salinity ~15) is

1 evidence of the occurrence of denitrification or other organic degradation processes,

2 as also evidenced by extremely high DIC (7147-8757 $\mu$mol L$^{-1}$) and TAlk (7364-9009

3 $\mu$mol L$^{-1}$).

4

5 **CO$_2$ parameters in the NSCS subterranean estuary**

6 Figure S3 shows the distribution of DIC, TAlk, pH, and partial pressure of CO$_2$

7 ($p$CO$_2$) versus salinity in the NSCS STE sampled in 2008 and 2010. DIC mostly

8 ranged from 2300 to 6000 $\mu$mol L$^{-1}$ in fresh groundwater, with an average of 4002

9 $\mu$mol L$^{-1}$ (Fig. S3A). The brackish groundwater had DIC values ranged from 2866 to

10 8757 $\mu$mol L$^{-1}$, with an average of 5078 $\mu$mol L$^{-1}$, which was higher than that in

11 fresh groundwater (Fig. S3A). TAlk had a distribution pattern similar to DIC, except

12 that it was lower than DIC in fresh groundwater (average of 3301$\mu$mol L$^{-1}$), but

13 higher in the high salinity zone (average of 6631 $\mu$mol L$^{-1}$; Figs. S3A and S3B).

14 Nevertheless, both DIC and TAlk in the groundwater were significantly higher than

15 those in the surface seawaters (DIC:~1909 $\mu$mol L$^{-1}$, TAlk:~2202 $\mu$mol L$^{-1}$), and the

16 overlying river waters (DIC:~1060 $\mu$mol L$^{-1}$, TAlk:~1007 $\mu$mol L$^{-1}$). High

17 concentrations of DIC and TAlk in groundwater but non carbonate dominant

18 sediments can be explained by strong bacterial activities. Aerobic organic matter

19 decomposition, denitrification, Mn and Fe oxide reduction, sulfate reduction, and

20 methanogenesis would produce ammonia and CO$_2$ simultaneously (Lovely and

21 Chapelle, 1995; Slomp and Van Cappellen, 2004; Chen et al., 2006). Good positive

22 relationship ($R^2$=0.90, n=9) between NH$_4^+$ and DIC in groundwater (Table S1, figure

1    not shown) provided evidence to support it. Another possible reason was that a great

2    number of liming additions has increased soil alkalinity in order to improve local

3    soil fertility and structure. The measured pH in fresh groundwater ranged from 6.19

4    to 7.35, which was lower than saline groundwater (7.38 to 7.84; Fig. S3C).

5    Obviously, the STE has lower pH than seawater. Partial $CO_2$ pressure ($pCO_2$) in

6    groundwater was pronouncedly different from the surface waters, ranging from 1030

7    to 61040 µatm (Fig. S3D), and was 3-150 times higher than the atmospheric $CO_2$.

8    The extremely high $pCO_2$ level has been observed in many groundwater systems,

9    such as the wetlands and salt marshes in Georgia and South Carolina (Cai et al.,

10   2003; Moore et al., 2006), the Herbert aquifer in Great Barrier Reef (Gagan et al.,

11   2002), and the shallow groundwater in Konza Prairie (Macpherson et al., 2008).

12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33

**References in supplementary material**

Appelo, C.A.J.: Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer, Water Resour. Res., 30, 2793-2805, 1994.

Beck, A. J., Tsukamoto, Y., Tovar-Sanchez, A., Huerta-Diaz, M., Bokuniewicz, H. J., and Sañudo-Wilhelmy, S. A.: Importance of geochemical transformations in determining submarine groundwater discharge-derived trace metal and nutrient fluxes, Appl. Geochem., 22, 477-490, 2007.

Cai, W.-J., Wang, Y.-C., Krest, J., and Moore, W. S.: The geochemistry of dissolved inorganic carbon in a surficial groundwater aquifer in North Inlet, South Carolina, and the carbon fluxes to the coastal ocean, Geochim.Cosmochim.Acta, 67, 631-639, 2003.

Cao, L., Wang, W.-M., Yang, Y., Yang, C.-T., Yuan, Z.-H., Xiong, S.-B., and James, D.: Environmental Impact of Aquaculture and Countermeasures to Aquaculture Pollution in China, Env. Sci. Pollut. Res., 14, 452-462, 2007.

Chen, C.-T. A., Wang, S.-L., Chou, W.-C., and Sheu, D. D.: Carbonate chemistry and projected future changes in pH and $CaCO_3$ saturation state of the South China Sea, Mar. Chem., 101, 277-305, 2006.

Gagan, M. K., Ayliffe, L. K., Opdyke, B. N., Hopley, D., Scott-Gagan, H., and Cowley, J.: Coral oxygen isotope evidence for recent groundwater fluxes to the Australian Great Barrier Reef, Geophys. Res. Lett., 29, 1982, doi: 10.1029/2002GL015336, 2002.

Harriet F. Carlyle, John H. Tellam, et al.: The use of laboratory-determined ion exchange parameters in the predictive modelling of field-scale major cation migration in groundwater over a 40-year period, J. Contam. Hydrol, 68:55-81, 2004.

Lovely, D. R., and Chapelle, F. H.: Deep subsurface microbial processes, Rev. Geophys., 33, 365-381, 1995.

Macpherson, G. L., Roberts, J. A., Blair, J. M., Townsend, M. A., Fowle, D. A., and Beisner, K. R.: Increasing shallow groundwater $CO_2$ and limestone weathering, Konza Prairie, USA, Geochim. Cosmochim. Acta., 72, 5581-5599, 2008.

Moore, W. S.: The subterranean estuary: a reaction zone of ground water and sea water, Mar. Chem., 65, 111-125, 1999.

Moore, W. S., Blanton, J. O., and Joye, S. B.: Estimates of flushing times, submarine groundwater discharge, and nutrient fluxes to Okatee Estuary, South Carolina, J. Geophys. Res., 111, C09006, doi:10.1029/2005JC003041, 2006.

Moore, W. S.: The Effect of Submarine Groundwater Discharge on the Ocean, Annu. Rev. Mar. Sci., 2, 59-88, 2010.

Slomp, C. P., and Van Cappellen, P.: Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact, J. Hydrol., 295, 64-86, 2004.

Swarzenski, P. W., Porcelli, D., Andersson, P. S., and Smoak, J. M.: The behavior of U and Th-series nuclides in the estuarine environment, Rev. Mineral Geochem., 52, 577-606, 2003.

Table S1. The location, temperature, salinity, major cations, dissolved oxygen (DO), radium activities, $CO_2$ parameters and nutrient concentrations for subterranean estuaries along the NSCS collected in 2008 and 2010. Sampling sites are shown in Fig 1.

| Sample ID | Salinity | Temp (℃) | Na+ | Mg2+ | Ca2+ (mmol kg-1) | DO % | ex224Ra* | 223Ra | 226Ra (dpm 100 L-1) | 228Ra | TAlk | DIC (µmol L-1) | pCO2 (matm) | pH | NH4+ | NO3-+NO2- | DIP | DSi (µmol L-1) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| a※ | 0.2 | 27.0 | - | - | - | 66 | 419.47±10.18 | 15.66±4.24 | 74.39±22.01 | 581.80±31.13 | 2925.4 | 3818.4 | 26.36 | 6.84 | - | - | - | - |
| b※ | 0.2 | 21.9 | - | - | - | 76 | 422.61±14.49 | 14.93±3.01 | 182.11±21.22 | 541.38±30.06 | 5025.7 | 5918.3 | 26.43 | 7.07 | 0.3 | 810.7 | 1.1 | 83 |
| c※ | 0.0 | 25.8 | - | - | - | 31 | 652.93±17.36 | 17.96±3.85 | 137.88±18.25 | 581.80±29.46 | 1579.2 | 3183.9 | 47.26 | 6.34 | 100.1 | 1009.7 | 0.7 | 194.1 |
| d※ | 0.0 | 20.8 | - | - | - | 28 | 216.12±8.86 | 5.67±2.03 | 65.07±6.18 | 183.82±17.13 | 1764.7 | 2341.1 | 16.99 | 6.84 | 2.5 | 1612.5 | 37.4 | 360.2 |
| Spring※ | 17.2 | - | - | - | - |  | 1195.23±35.14 | 60.46±15.59 | 160.65±21.92 | 422.23±30.97 | - | - | - | - | 1.1 | 610.6 | 1.7 | 194.1 |
| Xinxi# | 8.5 | 28.2 | 5.1 | 14.7 | 3.5 | 19 | 1718.21±4.13 | 56.17±4.15 | - | 872.12±37.51 | 2663.0 | 2866.4 | 6.31 | 7.38 | 59.9 | 52.6 | 0.1 | 213.7 |
| Dongshan# | 3.0 | 26.7 | 2.3 | 0.7 | 2.4 | 13 | 271.35±14.41 | 6.57±1.16 | - | 79.60±10.83 | 7109.8 | 7523.6 | 14.45 | 7.35 | 436.7 | - | - | 701.5 |
| Haimen# | 24.3 | 27.8 | 13.2 | 34.4 | 8.0 | 14 | 1368.13±2.33 | 56.13±6.55 | - | 585.51±29.64 | 3306.0 | 3203.4 | 1.03 | 7.82 | 89.3 | 5.56 | 0.8 | 75.6 |
| Haimen2# | 23.2 | 28.8 | 12.5 | 32.2 | 7.8 | 11 | 1072.26±73.58 | 41.59±5.79 | - | 523.35±24.53 | 3521.9 | 3414.2 | 1.10 | 7.84 | 50.6 | 6.84 | 0.2 | 80.6 |
| Huilai# | 0.0 | 27.8 | 0.3 | 0.1 | 0.2 | 45 | 61.71±5.17 | 3.63±1.14 | - | 30.16±12.55 | 380.7 | 900.8 | 15.46 | 6.19 | 1.6 | 87.64 | 0.1 | 243.3 |
| Luyuancun# | 3.0 | 26.8 | 2.4 | 0.8 | 2.2 | - | 897.22±1.59 | 31.43±3.42 | - | 395.67±20.75- | 5343.6 | - |  | 6.93 | 32.9 | 1043.9 | 0.1 | 273.6 |
| Shajiaowei# | 0.0 | 27.2 | 0.3 | 2.4 | 0.5 | - | 280.89±12.95 | 7.88±2.22 | - | 133.23±12.78- | 2278.4 | 4329.9 | 61.04 | 6.27 | 318.2 | 148.6 | 0.2 | 185.6 |
| Xiayang1# | 15.6 | 28.3 |  | - |  | - | 521.22±29.23 | 11.01±2.2 | - | 439.32±23.65 | 7364.5 | 7147.2 | 2.19 | 7.73 | 573.5 | 5.24 | 19.8 | 169.2 |
| Xiayang2# | 16.6 | 27.6 | 8.9 | 26.5 | 7.1 | - | 512.25±36.39 | 20.32±2.71 | - | 418.87±20.64 | 9008.9 | 8757.1 | 2.72 | 7.69 | 572.2 | 7.08 | 17.2 | 180.6 |

Superscript ※groundwater taken in Dec. 2008; # groundwater collected in Oct. 2010;

*ex224Ra denotes excess 224Ra, corrected for the ingrowth from 228Th;

pCO2 was calculated from DIC and TAlk using CO2SYS.XLS 14th version (HTTP:// www.ecy.wa.gov/programs/eap/models.html.)

**Figures Captions in Supplementary Material**

Fig S1. Correlation between $^{223}$Ra and ex $^{224}$Ra (excess $^{224}$Ra, corrected for the ingrowth from $^{228}$Th) activities in the northern South China Sea subterranean estuary collected in December 2008 and October 2010.

Fig S2. Concentrations of (A) ammonia ($NH_4^+$), (B) Nitrate and nitrite ($NO_3^- + NO_2^-$), (C) dissolved silicate (DSi) and (D) dissolved inorganic phosphate (DIP) plotted versus salinity in the northern South China Sea subterranean estuary both in December 2008 and October 2010.

Fig S3. Concentrations of (A) dissolved inorganic carbon (DIC), (B) total alkalinity (TAlk), (C) pH, (D) partial $CO_2$ pressure ($pCO_2$) plotted versus salinity in the northern South China Sea subterranean estuary both in December 2008 and October 2010.
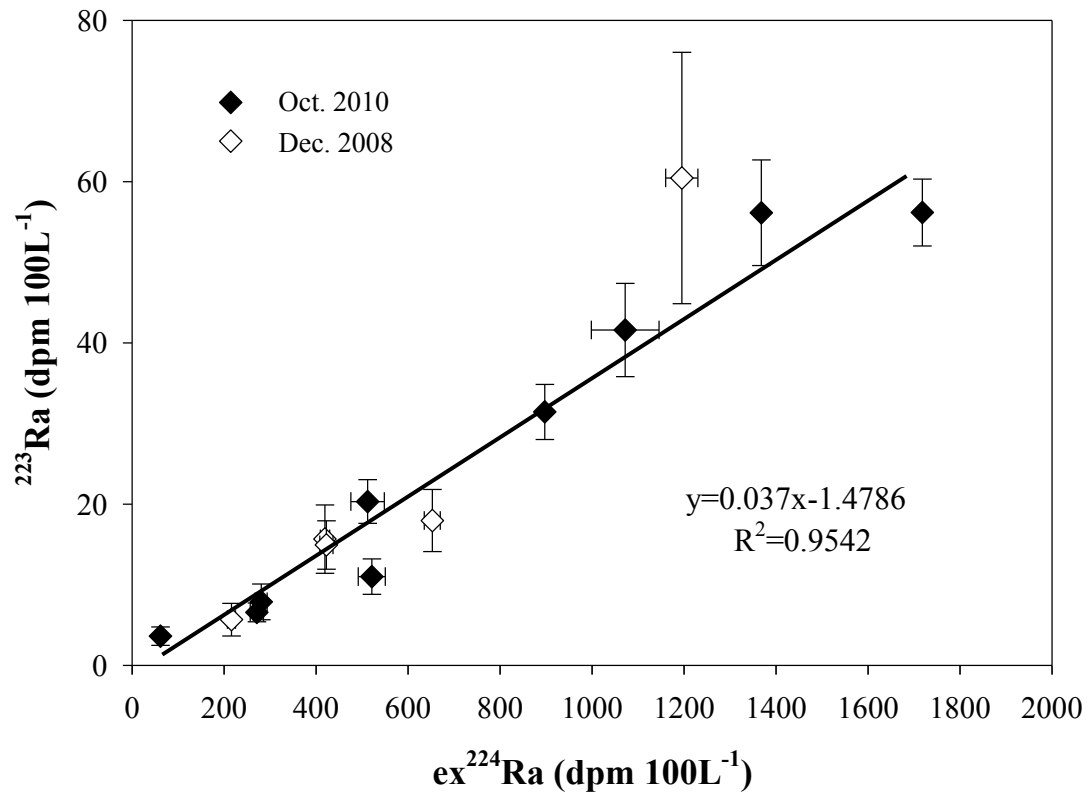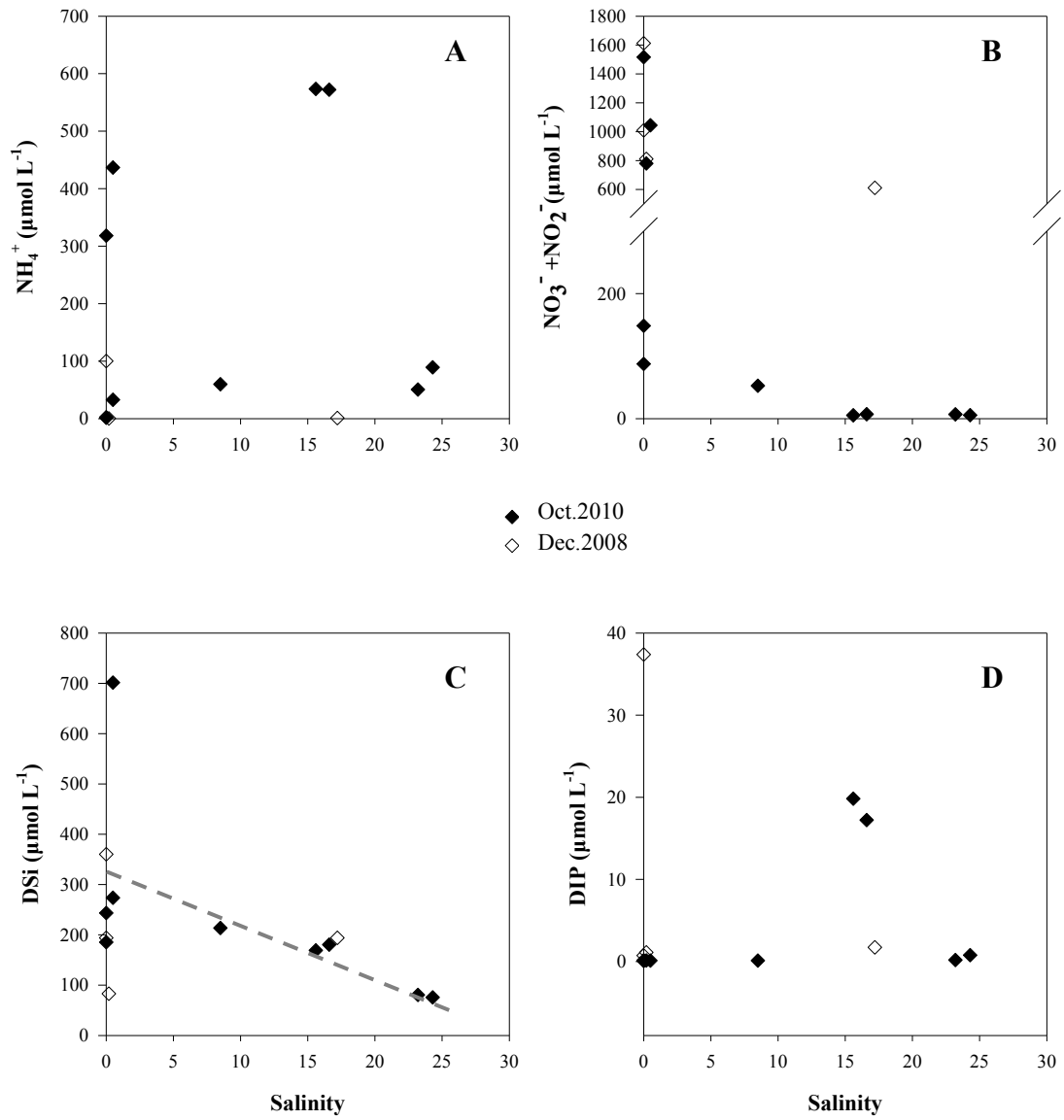
**Figure S1**

**Figure S2**

**Figure S3**